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Spectrochimica Acta Part A 71 (2008) 332–335
SPECTROCHIMICA ACTA PART A
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Determination of trace amount of oxalic acid with zirconium(IV)–(DBS-arsenazo) by spectrophotometry

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Received 28 March 2007; received in revised form 23 December 2007; accepted 27 December 2007

Abstract

A novel method is proposed for the determination of trace amount of oxalic acid in the present article. In 1.0 M hydrochloric acid medium, oxalic acid can react with the zirconium(IV) in Zr(IV)–(DBS-arsenazo) complex and replaces the DBS-arsenazo to produce a hyperchromic effect at 520 nm. The hyperchromic degree is proportional to the concentration of the oxalic acid added over a defined range. Based on this property, a new method for the spectrophotometric determination of trace oxalic acid was developed. Beer's law is held over the concentration range of 9.0×10^{-6} to 5.0×10^{-4} M for oxalic acid with a correlation coefficient of 0.9995. The apparent molar absorptivity of the method is $\varepsilon_{520\,nm} = 1.16 \times 10^3\ L\,mol^{-1}\,cm^{-1}$ and the detection limit for oxalic acid is 0.815 μg/mL. The developed method was directly applied to the determination of oxalic acid in tomato samples with satisfactory results.

Keywords: Oxalic acid; Zirconium(IV); DBS-arsenazo; Spectrophotometry

Oxalic acid is a common material in some food samples. It can form stable and precipitated calcium oxalate complex with calcium in the body. This not only hinders the absorption of calcium in human body, but also easily initiates urinary calculus. The excessive oxalic acid can influence the people's health [1]. Thus, the determination of the amount of oxalic acid in some samples such as fruits, etc., has very important practical significance. Although spectrophotometry [2,3], extraction-spectrophotometry [4], catalytic kinetic spectrophotometry [5–7], fluorimetry [8], catalytic fluorimetry [9] have been used for the determination of trace oxalic acid, the proposed methods have their own defects such as poor selectivity [2–9], time-consuming operation [4–7,9], expensive analytical instrument [8,9]. A few spectrophotometric, extraction- or catalytic-spectrophotometric methods for the determination of oxalic acid have been reported, but their selectivity is still poor [2–7]. Thus, there is a demand for an inexpensive, simple and selective procedure in order to obtain more accurate information about oxalate levels in some samples. It is of very interest to develop a simple and selective method for the determination of oxalic acid. DBS-arsenazo (DBS-ASA), 3-(2,6-dibromo-4-sulfophenylazo)-6-(2-arsenophenylazo)-4,5-dihydroxynaphthalene-2,7-disulfonic acid, is an azo dye reagent that has been used for the spectrophotometric determination of rare earths [10]. It is found in the present study that oxalic acid can replace the DBS-ASA in Zr(IV)–(DBS-ASA) complex, while the oxalic acid coordinates with the Zr(IV) to form a stable complex. The replaced DBS-arsenazo produces a hyperchromic effect at 520 nm. The hyperchromic degree is proportional to the concentration of the oxalic acid added over a defined range. Based on this property, a new, simple and selective method was developed for the determination of trace oxalic acid. Compared with other methods [2–9], the present method has the advantages of operation simplicity, rapidity and good selectivity. The method was directly used to determine trace oxalic acid in tomato samples with satisfactory results.

1. Experimental

1.1. Reagent and apparatus

Oxalic acid standard solution: 1.0×10^{-3} M working solution was prepared by dissolving 0.0315 g of oxalic acid (Beijing Chemical Plant) with water in a beaker. The solution was

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doi:10.1016/j.saa.2007.12.026

placed in a 250-mL calibrated flask, diluted up to the mark with distilled water, and mixed well. Another 1.0×10^{-4} M oxalic acid working solution was obtained by appropriate dilution of 1.0×10^{-3} M oxalic acid solution. Zr(IV) solution: 5.0×10^{-4} M Zr(IV) solution was prepared by dissolving 0.0403 g of $ZrOCl_2 \cdot 8H_2O$ (Shanghai Chemical Reagent Company) with 10 mL of 1 M nitric acid in a beaker, the solution was placed in a 250-mL calibrated flask, diluted up to the mark with distilled water and mixed well. DBS-Arsenazo (DBS-ASA, $C_{22}H_{15}AsBr_2N_4O_{14}S_3$) solution: 5.0×10^{-4} M working solution was prepared by dissolving 0.1073 g of DBS-ASA (Shanghai Changke Research Institute for Reagent) with distilled water in a beaker, placed in a 250-mL calibrated flask and diluted up to the mark with distilled water, and mixed well. A 10.0-M hydrochloric acid solution was prepared by appropriate dilution of its concentrated solution. All reagents were of analytical grade and the water was distilled water.

A 722S spectrophotometer (Shanghai Lingguang Technique Co., Ltd., China) with 1 cm cells was used in the experiment.

1.2. Procedure

A 1.0-mL of 10.0 M hydrochloric acid solution, 0.50 mL of 5.0×10^{-4} M Zr(IV) solution, 1.0 mL of 5.0×10^{-4} M DBS-arsenazo solution and an appropriate amount of oxalic acid standard solution were successively added into a 10-mL calibrated flask, respectively. The solution was diluted up to the mark with water and mixed well. After 25 min, the absorbance was measured in 1 cm cells at 500 nm against a corresponding reagent blank.

2. Results and discussions

2.1. Absorption spectra

The absorption spectra of the colored systems were drawn by using the general procedure and are shown in Fig. 1. The results showed that the maximum absorption peak of DBS-ASA is at 500 nm. The maximum absorption peaks of Zr(IV)–(DBS-ASA) complex and $H_2C_2O_4$ + Zr(IV) + (DBS-ASA) system against water are both at 520 nm. After oxalic acid was added to the Zr(IV)–(DBS-ASA) system, the absorbance of colored solution against water at 520 nm was increased. Because oxalic acid can coordinate with the Zr(IV) in the Zr(IV)–(DBS-ASA) complex, the DBS-ASA that is not complexed turns up in solution. The change of absorbance takes place. The maximum absorption peak of the $H_2C_2O_4$ + Zr(IV) + (DBS-ASA) colored system against the corresponding reagent blank is at 520 nm. Therefore, 520 nm was selected as measurement wavelength.

2.2. Effect of acidity

The experimental results showed when the amount of hydrochloric acid was 0.80–1.5 mL, the absorbance was maximum and constant over the concentration of 0.80–1.5 M hydrochloric acid. Outside this range, the sensitivity of the determination of oxalic acid is lower. Thus, 1.0 M hydrochloric acid solution was recommended as the acidity of color medium in experiments. A 1.0-mL of 10.0 M hydrochloric acid was added to control the acidity.

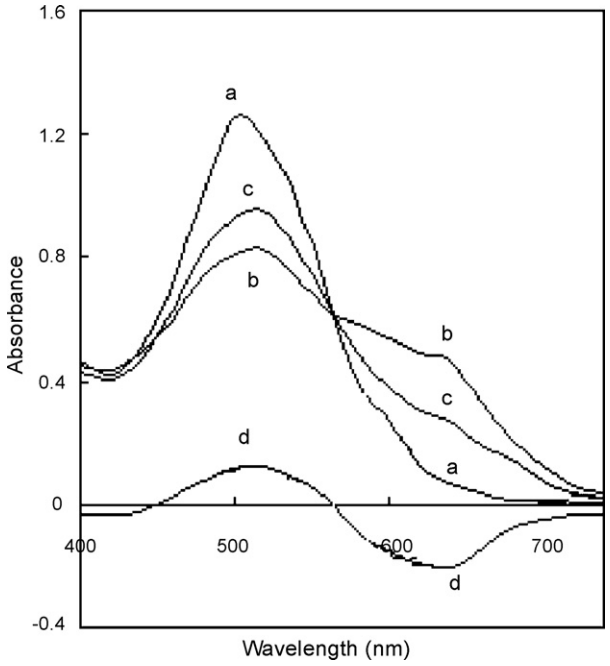

Fig. 1. Absorption spectra: (a) DBS-ASA (against H_2O); (b) (DBS-ASA)–Zr(IV) (against H_2O); (c) $H_2C_2O_4$–(DBS-ASA)–Zr(IV) (against H_2O); (d) $H_2C_2O_4$–(DBS-ASA)–Zr(IV) (against corresponding reagent blank). $[H_2C_2O_4] = 1.05 \times 10^{-4}$ M; [DBS-ASA] = 5.0×10^{-5} M; [Zr(IV)] = 2.5×10^{-5} M; [HCl] = 1.0 M.

2.3. Effect of the amount of DBS-arsenazo

The experiments showed that over the range of 0–0.90 mL of 5.0×10^{-4} M DBS-arsenazo the absorbance gradually raised with increasing the amount of DBS-ASA. When the amount of DBS-ASA solution was 0.90–1.2 mL and the concentration of DBS-ASA was 4.5×10^{-5} to 6.0×10^{-5} M, the absorbance was a maximum and constant. In the present experiment 1.0 mL of 5.0×10^{-4} M DBS-ASA solution was selected. The concentration of DBS-ASA was 5.0×10^{-5} M.

2.4. Effect of the amount of zirconium(IV) solution

The effect of the amount of zirconium(IV) was tested. The results showed that the absorbance gradually increased with increasing the concentration of zirconium(IV) over the concentration range of $(0–2.0) \times 10^{-5}$ M. When the zirconium(IV) concentration was 2.0×10^{-5} to 1.0×10^{-4} M, the absorbance was maximum and constant. In the experiments, the concentration of zirconium(IV) was selected to be 2.5×10^{-5} M and a 0.50-mL of 5.0×10^{-4} M zirconium(IV) solution was employed.

Table 1
Analytical results of samples

Sample	Found (mg/g)	Average (mg/g)	R.S.D. (%)	Added (10^{-5} M)	Recovered (10^{-5} M)	Recovery (%)	Contrast method [5] (mg/g)
No. 1	1.22, 1.25, 1.20, 1.20, 1.21, 1.26	1.22	2.14	5.00	4.96	99.2	1.23
No. 2	1.62, 1.64, 1.60, 1.65, 1.62, 1.60	1.62	1.27	5.00	4.98	99.6	1.62

2.5. Effect of temperature

For the $H_2C_2O_4 + Zr(IV) + (DBS\text{-}ASA)$ system, the absorbance attained maximum and constant at room temperature ($20 \pm 5\,^{\circ}C$). Outside this range of temperature, the sensitivity decreased.

2.6. Stability of the chromogenic system

After all reagents were mixed, the absorbance of system reached a maximum in 25 min and the colored system reached equilibrium. The variation of absorbance of the system was less than 5% in 12 h and the system kept stable at room temperature ($20 \pm 5\,^{\circ}C$).

2.7. Composition of the complex and mechanism of the reaction

The complex ratio of Zr(IV)–(DBS-ASA), determined by using molar ratio and the equimolar continuous variation methods, was 1:1.

The chemical reactions, which can be expected to take place in the corresponding systems, can be expressed as follows:

$$ZrOCl_2 + C_{22}H_{15}AsBr_2N_4O_{14}S_3 \rightarrow Zr(C_{22}H_{11}AsBr_2N_4O_{14}S_3) + 2HCl + H_2O \quad (1)$$

$$Zr(C_{22}H_{11}AsBr_2N_4O_{14}S_3) + 2H_2C_2O_4 \rightarrow Zr(C_2O_4)_2 + C_{22}H_{15}AsBr_2N_4O_{14}S_3 \quad (2)$$

Table 2
Comparison of the present method with other reported methods

Analytical method	System	Linear range (μg/mL)	Detection limit (μg/mL)	Remark	Analytical application	References
Spectrophotometry	Oxalic acid-zinc-phenylhydrazine hydrochloride	0–20	0.1	Poor selectivity	Water	[2]
Spectrophotometry	Oxalate-zirconium(IV)-quercetin	0–5.0	0.25	Poor selectivity	–	[3]
Extraction-spectrophotometry	Oxalate-vanadium(V)-mandelohydroxamic acid (extraction solvent is toluene solution of trioctylmethylammonium chloride/adogen 446)	2–8	0.5	Extraction is needed and operation is time-consuming	Urine, blood serum	[4]
Catalytic kinetic spectrophotometry	Oxalic acid-rhodamine B-potassium dichromate	0.40–6.0	0.252	Metal ions, i.e. Cr^{3+}, Bi^{3+}, La^{3+}, Eu^{3+}, Y^{3+} interfere and selectivity is poor. Heating is needed	Spinach, tea, urine	[5]
Catalytic kinetic spectrophotometry	Oxalic acid-chromium(III)-alizarin red S	0–140.8	3.86	Heating time is 1 h and operation is time-consuming. Poor sensitivity and selectivity present	Water	[6]
Catalytic kinetic spectrophotometry	Oxalic acid-iron(II)-iodide-bromate	0.10–7.0	0.080	Poor selectivity	Tap water, river water, spinach, mushroom	[7]
Fluorimetry	2,2,7,7,12,12,17,17-Octamethyl-21,22,23,24-tetraoxaqyaterene-Mg	0.55–73.9	0.074	Poor selectivity	Spinach, urine	[8]
Catalytic fluorimetry	Oxalic acid-rhodamine 6G-potassium dichromate	0.80–14.0	–	Sensitive but less selective. Heating is needed	Spinach, urine	[9]
Present method	Oxalic acid-Zr(IV)–(DBS-arsenazo)	0.81–45.0	0.815	Simple and highly sensitive, free from interference of common ions. No heating is needed	Tomato	Present paper

Here, Zr(IV) first reacts with DBS-ASA to produce $Zr(C_{22}H_{11}AsBr_2N_4O_{14}S_3)$ product. Then, $H_2C_2O_4$ replaces the $C_{22}H_{11}AsBr_2N_4O_{14}S_3$ in the $Zr(C_{22}H_{11}AsBr_2N_4O_{14}S_3)$ to produce $Zr(C_2O_4)_2$. The reason, why the replacement reaction takes place, was that the stability constant of $Zr(C_2O_4)_2$ is expected to be larger than the one of $Zr(C_{22}H_{11}AsBr_2N_4O_{14}S_3)$.

2.8. Calibration curve

Under the optimum experimental conditions, a linear relationship was shown over the concentration range of 9.0×10^{-6} to 5.0×10^{-4} M for oxalic acid. The regression equation for calibration graph was: $A = 3.30 \times 10^2\,C + 0.0884$ (C:M), with a correlation coefficient 0.9995, and the apparent molar absorptivity is $\varepsilon_{520\,nm} = 1.16 \times 10^3\,L\,mol^{-1}\,cm^{-1}$. The precision of the present method was evaluated by determining 2.0×10^{-4} M oxalic acid standard solution 11 times with a relative standard deviation of 0.98%. The limit of detection as defined by IUPAC [11] and the limit of quantification [12] were found to be 0.815 μg/mL and 2.39 μg/mL, respectively.

2.9. Interference study

The effect of a series of 54 diverse inorganic and organic substances on the determination of 2.0×10^{-4} M oxalic acid was checked. The tolerance limits (mass multiple, *m/m*) of the common ions tested (causing <±5% relative error) are summarized as follows: K^+ (700); Na^+ (500); Li^+ (400); NH_4^+ (100); Ag^+ (0.03); Mn^{2+} (400); Fe^{2+} (40); Cu^{2+} (4); Cd^{2+}, Sn^{2+} (1); Ba^{2+}, Ni^{2+} (0.3); Zn^{2+}, Co^{2+} (0.2); Ca^{2+}, Mg^{2+} (0.05); Pb^{2+} (0.007); Al^{3+} (400); Fe^{3+} (5); Cr^{3+} (0.8); Bi^{3+} (0.2); Y^{3+} (0.07); La^{3+} (0.05); Th^{4+} (0.005); Br^-, I^-, NO_3^- (100); F^-, NO_2^- (5); VO_3^- (0.4); WO_4^- (0.1); BrO_3^- (0.007); MnO_4^- (0.0005); SO_4^{2-} (100); $S_2O_7^{2-}$ (4); $Cr_2O_7^{2-}$, SiO_3^{2-} (2); PO_4^{3-} (8); $Mo_7O_{24}^{6-}$ (0.07); EDTA (ethylene diamine tetraacetic acid) (8); citric acid, urea (500); glucose (400); ascorbic acid (70); lysine, alanine (7); acetic acid, leucine, serum albumin (5); glycocoll, bovine red albumin (4); tartaric acid, malic acid (2); salicylic acid (1).

3. Applications

The applicability of the proposed method has been checked in two tomato samples. A 50.0000 g of tomato sample was soaked for 30 min with 250 mL of boiling water at 100 °C in a beaker. After the solution was cooled, it was filtered three times and transferred into a 250-mL calibrated flask. An aliquot of the above testing solution was placed into a 10-mL calibrated flask and then the content of oxalic acid was determined according to the general procedure. The analytical results are listed in Table 1. From the table it can be seen that the analytical results of the present method were in excellent agreement with those by oxalic acid-rhodamine B-potassium dichromate catalytic kinetic spectrophotometry [5]. The relative standard deviation of six parallel determinations for the samples and recovery were 1.27–2.14% and 99.2–99.6%, respectively. The mean relative standard deviation and mean recovery were 1.71% and 99.45%, respectively. The analytical results obtained were quite satisfactory.

4. Comparison with other methods

A comparison of the present procedure with other methods is listed in Table 2. From the table it can be seen that the present method has the advantages of operation simplicity, rapidity and low analytical cost. The method possesses distinct advantages over existing methods with respect to sensitivity, selectivity, speed, accuracy, precision and ease of operation. It has much more practical value for the determination of trace oxalic acid.

5. Conclusions

A new spectrophotometric method for the determination of trace amount of oxalic acid was proposed with Zr(IV)–(DBS-arsenazo) complex in this paper. The linear range of determination of oxalic acid is 9.0×10^{-6} M to 5.0×10^{-4} M. The detection limit of the present method for oxalic acid is 0.815 μg/mL. The proposed method has been applied to the determination of oxalic acid in tomato samples with satisfactory results. The present procedure has the advantages of the operation simplicity, rapidity and low analytical cost. It is simple, highly sensitive, free from interference of common ions and has much more practical value for the determination of trace oxalic acid compared with other methods [2–9].

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